

# The Effect of Surface Ligands on Optical and Electronic Spectra of Semiconductor Nanoclusters

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Using Density Functional Theory (DFT), we investigate the impact of passivating ligands on morphology, electronic structure, and optical response of CdSe QDs a topic of general interest due to the recent focus on QD-based solar cells, light-emitting diodes, field-effect transistor, etc. Specifically, we consider the Cd<sub>33</sub>Se<sub>33</sub> cluster passivated by amine and phosphine oxide ligands. These clusters already overlap in size with the smallest synthesized CdSe QDs, while molecules model the most common ligands used for the surface passivation of CdSe QDs. Our calculations demonstrate significant surface reorganization both for the bare cluster and for the cluster capped by ligands. We observe strong surface-ligand interactions leading to substantial charge redistribution and polarization effects on the surface. These effects result in the development of hybridized states, for which the electronic density is spread over the CdSe cluster and the ligands. Neither the ligand nor hybridized molecular orbitals appear as trap states inside or near the band gap of the QD. Instead, being optically dark, dense hybridized states from the edges of the valence and the conduction bands could open new relaxation channels for high energy photoexcitations. Comparing QDs passivated by different ligands, we found that hybridized states are denser at the edge of the QD conduction band of the cluster ligated with phosphine oxide molecules than that with primary amines. Such a different manifestation of ligand binding may potentially lead to faster electron relaxation in QDs passivated by phosphine oxide than by amine ligands. The efficiency of such relaxation channel would certainly depend on the electron-phonon interactions and non-adiabatic coupling, which are also addressed in our studies.